INFLUENCE OF THE ENERGY LEVELS ON THE EFFICIENCY OF ORGANIC BULK HETEROJUNCTION SOLAR CELLS

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ABSTRACT: We investigate the influence of the energy levels on the power conversion efficiency of a P3HT:PCBM and a MEH-PPV:PV bulk heterojunction cell. We calculate the upper-limit for the efficiency, and make realistic assumptions to predict efficiencies obtainable in the near future. The ideal position of the energy levels of donor and acceptor are obtained from these calculations, giving an idea how the ideal organic solar cell should look like. Also the expected efficiency gain by tuning energy levels, bandgap or absorption window can be derived from the simulations.
Our calculations show that, for a bulk heterojunction cell with P3HT as donor, reaching efficiencies of 10 % is only possible by adapting the LUMO-level of the electron acceptor. Further, lowering the bandgap of the donor would only increase the efficiency if also the absorption window increases. We also demonstrate that MEH-PPV is not a good donor for organic solar cells, because of the high bandgap. The results indicate that, by changing the energy levels, organic cells could have the potential for reaching higher efficiencies , which is a necessity for future commercial applications.

Keywords: modelling, organic solar cell, fundamentals

1 INTRODUCTION

Photovoltaic solar cells based on organic compounds are promising candidates for solar energy conversion. They have the potential for cost effectiveness, mechanical flexibility and easy processing. However, in order to compete with the traditional inorganic cells, power conversion efficiencies of more than 10% are a necessity. Nowadays, efficiencies up to 5% are reached [1] and the question about the limits for the attainable efficiency of organic cells arises.

In this article, we investigate the influence of the energy levels on the power conversion efficiency of a bulk heterojunction cell with respectively P3HT (poly-[3-hexylthiophene]) and MEH-PPV (poly-[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene]) as electron donor, and respectively PCBM ([6,6]-phenyl C61-butyric acid methyl ester) and PV (phenylene vinylene) as electron acceptor. We calculate the upper-limit for the efficiency, and make realistic assumptions to predict efficiencies obtainable in the near future. The ideal position of the energy levels of donor and acceptor are obtained from these calculations, giving an idea how the ideal organic solar cell should look like. Also the expected efficiency gain by tuning energy levels, bandgap or absorption window can be derived from the simulations.

2 ASSUMPTIONS

For our simulation, we make the following fundamental assumptions: (i) only one material absorbs: the *p*-type component (or electron donor). The *n*-type component (or electron acceptor) does not absorb any light. (ii) Every photon with an energy $h\nu$ higher than the bandgap $E_{g,p}$ is absorbed, with the bandgap defined as the difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the donor material. (iii) not any photon with an energy $h\nu$ lower than this bandgap $E_{g,p}$ is absorbed.

The distance between the HOMO of the donor and the LUMO of the acceptor is considered as the thermodynamic limitation for the useful energy. This value is often called the interface bandgap $E_{g,i}$. We assume that (iv) every absorbed photon leads to a useful energy $E_{g,i}$. This last assumption means that the absorbed photon leads finally to a free electron and a free hole, with an energy difference of $E_{g,i}$ between them. In this case, the maximum efficiency $\eta_{\max}$ is given by:

$$\eta_{\max} = \frac{E_{g,i}\int_{E_{g,p}}^{\infty} N(E)\,dE}{\int_{0}^{\infty} E\,N(E)\,dE}$$

with $N(E)$ the photon flux. For all our simulations, we use the AM 1.5 experimentally measured solar spectrum [2]. Notice that the denominator is a constant, i.e. the incident photon power density of the solar spectrum. The efficiency increases linearly with the interface bandgap $E_{g,i}$. In this ideal scenario, the open circuit voltage V_{oc} will be given by $E_{g,i}/q$, the fill factor *FF* equals unity, as well as the quantum efficiency *QE* for wavelengths lower than the cut-off wavelength $\lambda_{g,p}$ (corresponding with $E_{g,p}$).

3 P3HT:PCBM

First, we consider the organic solar cell with one of the highest efficiencies, namely the bulk heterojunction solar cell with P3HT as electron donor and the widely used PCBM as electron acceptor. The maximum efficiency reported for this cell is 4.9 % [1]. With the ideal assumptions mentioned above, calculations show that the maximum efficiency $\eta_{\max}$ that can be reached is 19.6 % for cells with an absorption window of at least 300 nm (Fig. 1 for definition of terms). For smaller absorption windows of e.g. 200 nm and 100 nm, the

maximum efficiency η_{max} is respectively 16.8 % and 9.2 %.

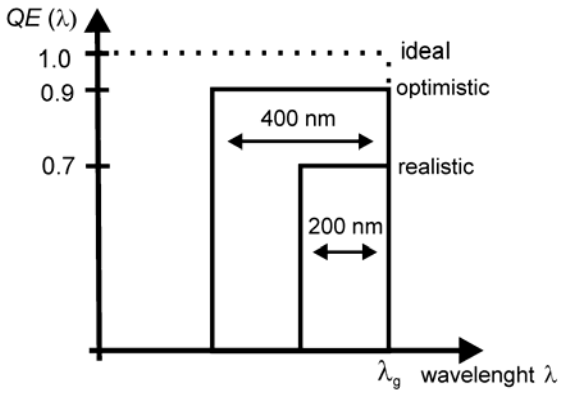

Figure 1: Definition of terms: absorption window; ideal (full absorption window), optimistic and realistic scenario for absorption and quantum efficiency QE. The cut-off wavelength λ_g corresponds with the bandgap $E_{g,p}$.

To estimate the obtainable efficiency in a less ideal situation, we assume two scenarios. In the first scenario, we assume the following realistic values [3], which are with the current state of technology nowadays reached in organic photovoltaics, like e.g. in the P3HT/PCBM bulk heterojunction. We assume an absorption window of 200 nm, a quantum efficiency *QE* of 70 %, a fill factor *FF* of 60 %, and a voltage factor *f*:

$$f = \frac{q \cdot V_{oc}}{E_{g,i}}$$

of 60 %. This results in a maximum attainable efficiency of 4.2 %. For an absorption window of minimum 300 nm, this value reaches 5.0 %. In the second scenario, we consider optimistic values, which are credible to be achieved in the future (i.e. an absorption window of 300 nm, *QE*=90 %, *FF*=70 %, *f*=70 %). Then, an efficiency of 8.6 % becomes possible for the P3HT/PCBM cell.

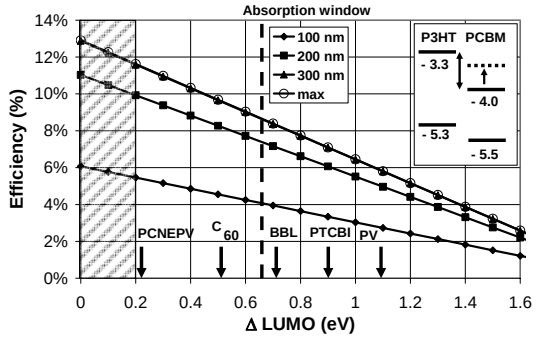

Figure 2: The maximum attainable efficiency as a function of the difference between the LUMO's of donor and acceptor, for the values of the optimistic scenario. The dotted line indicates the P3HT:PCBM cell. The values of the energy levels are given in the inset in eV. In the hatched area, exciton dissociation is not any more possible, because of the too low LUMO-difference. As example, the positions of other materials, which can be used as electron acceptor with P3HT, are given.

In organic bulk heterojunction solar cells, light absorption does not lead immediately to free charge carriers, but an exciton is created. A necessary condition for efficient dissociation of the created excitons is that the difference between the LUMO's of the donor and acceptor is higher than the exciton binding energy. Thus, without a sufficient energy difference between the LUMO's of both materials, the solar cell can not work. The value of the exciton binding energy in different materials is a subject of discussion, values between 0.1 eV and 2 eV are published [4]. The surplus of this necessary minimum of the LUMO-difference corresponds with an energy loss.

In Fig. 2 we start from the P3HT/PCBM bulk heterojunction solar cell in the optimistic scenario (dotted line in Fig. 2), and change the electron acceptor by varying the LUMO of the acceptor. The lower the difference between the LUMO's of donor and acceptor, the higher the interface bandgap $E_{g,i}$, the less energy is lost and thus the higher the efficiency. Each additional difference of 0.1 eV between the LUMO's results approximately in an additional two thirds absolute efficiency loss. However, because of the necessary exciton dissociation, a certain LUMO-difference is necessary. We assume that for the organic solar cell a difference of 0.2 eV between the LUMO's is necessary. This value was put forward in an empirical study as a threshold necessary for exciton dissociation [5]. By optimising the position of the LUMO energy level of the acceptor, a relative efficiency gain of 37 % can be achieved. Also notice that by increasing the absorption window from 200 nm to 300 nm, the efficiency rises relatively by 16 %. A bigger progress can be made by adapting the LUMO of the acceptor. With a full absorption window, the 10 % efficiency becomes possible. In the realistic scenario, an efficiency of 11.6 % is possible by changing the LUMO of the acceptor.

As example, the positions of other materials, which can be used as electron acceptor in a P3HT bulk heterojunction, are indicated on Fig. 2. However, one can not conclude that for example C_{60} would be a better acceptor than PCBM, because our calculations only take into account the position of the energy levels, and not other important material properties like morphology and charge carrier mobility.

In Fig. 3 we start again from the P3HT/PCBM bulk heterojunction solar cell in the optimistic scenario, but now we change the electron donor by varying the LUMO of the donor. If we lower the LUMO of the donor, the bandgap $E_{g,p}$ decreases, and more photons from the solar spectrum can be absorbed. However, by lowering the bandgap $E_{g,p}$, also the interface bandgap $E_{g,i}$ decreases, resulting in a lower useful energy per photon. Therefore, the optimum bandgap will be a compromise between photon absorption (current) and useful energy (voltage). We notice that with a full absorption window, the power conversion efficiency can increase from 9.0 % to 15.1 % by lowering the bandgap. However, when we consider a realistic absorption window of 200 nm, almost no efficiency gain can be achieved by lowering the bandgap. Thus lowering the bandgap without increasing the absorption window is useless. As example, the positions of other materials, which can be used as electron donor in a bulk heterojunction cell with PCBM, are indicated in Fig. 3. In the realistic scenario, a maximum efficiency of 9.4 % can be reached with a donor with bandgap 1.5 eV.

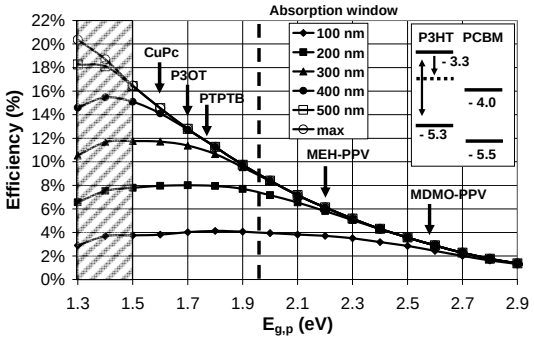

Figure 3: The maximum efficiency as a function of the bandgap $E_{g,p}$ of the donor, for the values of the optimistic scenario. The dotted line indicates the P3HT:PCBM cell. The values of the energy levels are given in the inset in eV. In the hatched area, exciton dissociation is not any more possible. As example, the positions of other materials, which can be used as electron donor in a bulk heterojunction cell with PCBM, are indicated.

We now combine the effect of changing the bandgap and the LUMO-difference. We vary the bandgap of the donor, but at the same time keep the difference between the LUMO of donor and acceptor constant on the empirical threshold of 0.2 eV (Fig. 4). Notice that with the realistic absorption window of 200 nm for P3HT/PCBM cells, the bandgap of P3HT is already optimal. Only when considering higher absorption windows, lowering the bandgap leads to an increase in efficiency. In the optimistic scenario, by tuning the LUMO's of both donor and acceptor, the maximum attainable efficiency η_{max} with an absorption window of 300 nm is 13.2 %, reached for an bandgap $E_{g,p}$ of 1.75 eV. Increasing this efficiency would require firstly a wider absorption window, and secondly a lower bandgap.

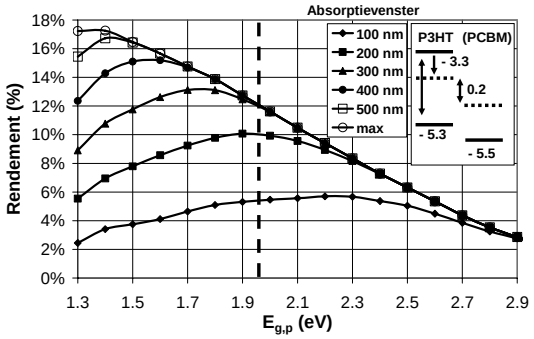

Figure 4: The maximum efficiency as a function of the bandgap $E_{g,p}$ of the donor, with the LUMO-difference equal to 0.2 eV and for the values of the optimistic scenario. The dotted line indicates the P3HT:PCBM cell. The values of the energy levels are given in the inset in eV.

3 MEH-PPV:PV

We now consider a bulk heterojunction solar cell with a higher bandgap $E_{g,p}$ than P3HT, namely the MEH-PPV/PV bulk heterojunction cell. The record for the efficiency of this cell is 1.55 % [6]. The highest efficiency that can be reached with this material combination is 8.5 % in the ideal scenario described above. If we consider our realistic and optimistic scenario, a maximum efficieny of respectively 2.0 % and 3.8 % is possible. These low efficiencies indicate that MEH-PPV:PV is not a good material combination for organic solar cells.

The reason for this low efficieny is the LUMO-difference between the donor and acceptor. The energy loss because of this difference is higher than with the P3HT-PCBM cell (see inset Fig. 5). Because of this, a much higher relative efficieny gain can be achieved by adapting the LUMO-level of the acceptor. For example, the efficiency increases relatively with 70 % by decreasing the LUMO-difference to the optimal size of 0.2 eV. This leads in our realistic scenario to an efficiency of 5.1 % by increasing the LUMO of the acceptor. In the optimistic scenario (Fig. 5), the efficieny rises from 3.8 % with PV as acceptor, to 9.4 % with an acceptor with optimised LUMO (i.e., an energy level of 0.2 eV lower then the LUMO of MEH-PPV).

Also notice on Fig. 5 that an absorption window of 200 nm is already sufficient for an (almost) maximum efficiency. The reason is the big bandgap of the absorber ($E_{g,p}$ = 2.2 eV). The consequence is that only photons with a wavelength lower then 560 nm can be absorbed. Therefore, the absorption window reaches quickly the border of 300 nm. Below 300 nm, there is not much energy available from the solar spectrum. Also in this material combination, more efficiency gain can be achieved by changing the LUMO, then by broaden the absorption window.

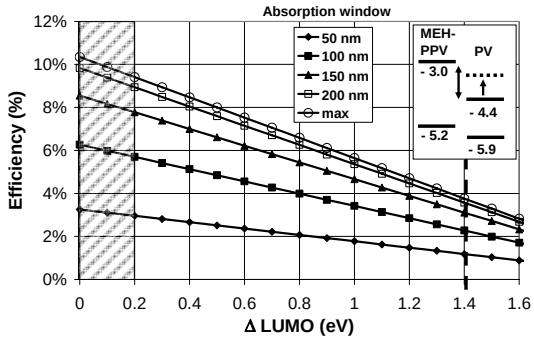

Figure 5: The maximum attainable efficiency as a function of the difference between the LUMO's of donor and acceptor, for the values of the optimistic scenario. The dotted line indicates the MEH-PPV:PCBM cell. The values of the energy levels are given in the inset in eV. In the hatched area, exciton dissociation is not any more possible, because of the too low LUMO-difference.

4 CONCLUSIONS

Our calculations show that, for a bulk heterojunction cell with P3HT as donor, reaching efficiencies of 10 % is only possible by adapting the LUMO-level of the electron acceptor. Further, lowering the bandgap of the donor would only increase the efficiency if also the absorption window increases. We also demonstrate that MEH-PPV is not a good donor for organic solar cells, because of the high bandgap.

The results indicate that, by changing the energy levels, organic cells could have the potential for reaching higher efficiencies , which is a necessity for future commercial applications.

5 ACKNOWLEDGEMENTS

The IWT SBO-project 030220 “NANOSOLAR” funded by the Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT).

6 REFERENCES

[1] M. Reyes-Reyes, K. Kim, D.L. Carroll, Appl. Phys. Lett. 87, (2005) 083506

[2] Hulström, Bird and Riordan, Solar Cells, 15, (1985) 365

[3] Solar Cell Efficiency Tables (version 28), Progress in Photovoltaics, 14, p.455, august 2006

[4] P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys, 93, (2003) 3693

[5] B. Minnaert, M. Burgelman, Eur. Phys. J. Appl. Phys. 38, (2007) 111

[6] J. Nakamura, C. Yokoe, K. Murata, and K. Takahashi, J. Appl. Phys, 96 (2004) 6878